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(Isocyanide)gold(I) Thiosalicylates: Supramolecular Assembly Based on both Auriophilic and Hydrogen Bonding

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*Summary: Reaction of (RNC)AuCl [R = tert-butyl (**1a**), mesityl (**1b**)] with sodium thiosalicylate in the two-phase system water/dichloromethane gives high yields of the corresponding (isocyanide)gold(I) thiosalicylates (**2a**,**b**). The solid-state structures of **2a**,**b** have been determined by X-ray diffraction studies. The supramolecular structure of both compounds is governed by Au--Au interactions [**2a**, Au--Au 3.157(2) Å; **2b**, Au--Au 3.3186(5) Å] and hydrogen bonding through the carboxylic acid groups.*

From extensive studies in the structural chemistry of gold(I) compounds it has been recognized that self-assembly of species L−Au−X (L = neutral donor, X = anionic ligand) through Au--Au contacts ("auriophilicity") is a general phenomenon determining many solid-state structures of such compounds.[1] The energies of the individual Au--Au interactions are in the order of 6−11 kcal/mol,[2] resembling closely the energetics of hydrogen bonding.[1a] This resemblance of auriophilic and hydrogen bonding suggested that there should be cases where both phenomena synergistically codetermine the assembly mode of solid-state structures. After a number of experiments, where the results failed to corroborate this assumption,[3] we are now able to present two examples with L representing isocyanide and X thiolate ligands.

The reactions of (dimethyl sulfide)gold(I) chloride with *tert*-butyl or mesityl isocyanide afford high yields of the corresponding (RNC)AuCl complexes (**1a**,**b**) as air-stable, colorless, crystalline materials.[4] These precursors are readily converted into the thiosalicylates (**2a**,**b**) by reaction with sodium thiosalicylate in the two-phase system water/dichloromethane.[5]

$$\mathrm{(RNC)AuCl + 2\text{-}(NaS)C_6H_4COOH \rightarrow 2\text{-}[(RNC)AuS]C_6H_4COOH + NaCl}$$

The products are again colorless, crystalline compounds stable to air and moisture and with high melting points (**2a**, 148 °C; **2b**, 226 °C with decomposition). Their composition is readily confirmed by analytical data,[5] but these do not exclude the presence of isomeric ionic systems of the general formula $[L_2Au]^+[AuX_2]^-$.[6] The IR absorptions for ν(NC) of the solids (**2a**, 2234 cm^{-1}; **2b**, 2200 cm^{-1}) indicate standard isocyanide coordination to gold(I) centers, and broad ν(OH) bands (**2a**, 2550−3300 cm^{-1}; **2b**, 2520−3200 cm^{-1}) are proof for strong hydrogen bonding of the carboxylate units in the crystals. The NMR spectra of solutions of the compounds in dichloromethane or chloroform show all resonances in the correct molar ratio 1:1 of L and X components,[5] but this result also gives no clue as to the structures. The solid-state structures were therefore determined by single-crystal X-ray diffraction studies.

Compound **2a** crystallizes in the orthorhombic space group *Pbca* with $Z = 16$ formula units in the unit cell. There are two crystallographically nonequivalent molecules in the asymmetric unit, which both have a quasi-linear C−N−C−Au−S skeleton extending from the central atom of the *tert*-butyl group to the sulfur atom of the thiol (Figure 1).[7−9] There is a short intermolecular auriophilic Au--Au contact [Au1--Au2 3.157(2) Å] which leads to pairs of molecules with a dihedral angle S1−Au1−Au2−S2 = 47.5°. The thiosalicylate ligands

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(5) Preparation of **2a**,**b**: The RNCAuCl complex was dissolved in dichloromethane (5 mL) and added to an equimolar amount of sodium thiosalicylate dissolved in water (5 mL). After the mixture was stirred for 3 h, the water layer was removed, the CH_2Cl_2 layer was evaporated to dryness, and the colorless residue was crystallized from a tetrahydrofuran/pentane mixture. **2a** (0.177 g, 65% yield) was obtained from ^{t}BuNCAuCl (0.198 g, 0.63 mmol) and 2-(NaS)C_6H_4COOH (0.111 g, 0.63 mmol). **2b** (0.123 g, 0.25 mmol) was obtained from MesNCAuCl (0.141 g, 0.37 mmol) and 2-(NaS)-C_6H_4COOH (0.066 g, 0.38 mmol). Spectroscopic and analytical data for **2a**: ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 13.10 (br s, COOH), 8.28 (d, $J = 8.0$ Hz, Ph-H^3), 7.63 (d, $J = 7.3$ Hz, Ph-H^6), 7.18−7.34 (m, Ph-H^4, H^5), 1.53 (s, *tert*-butyl); ^{13}C NMR ($CDCl_3$, 100.54 MHz) δ 167.6 (s, COO), 139.5 (br s, NC), 137.8 (s, C^4), 137.3 (s, C^2), 133.1 (s, C^6), 131.7 (s, C^3), 131.3 (s, C^1), 126.1 (s, C^5), 59.1 (s, $C(CH_3)_3$), 29.6 (s, CH_3); IR (KBr) ν_{COO-H} 3300−2550 (s), ν_{NC} 2234 (s), $\nu_{C=O}$ 1718 (s) and 1682 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{14}NAuO_2S$: C, 33.3; H, 3.3; N, 3.2. Found: C, 33.2; H, 3.1; N, 3.1. Mp: 148 °C. Spectroscopic and analytical data for **2b**: ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 13.00 (br s, COOH), 8.28 (d, $J = 7.9$ Hz, Ph-H^3), 7.69 (d, $J = 7.6$ Hz, Ph-H^6), 7.22−7.33 (m, Ph-H^4, H^5), 2.41 (s, o-CH_3), 2.31 (s, p-CH_3); because of the low solubility of **2b**, no ^{13}C-NMR spectrum was recorded; IR (KBr) ν_{COO-H} 3300−2520 (s), ν_{NC} 2200 (s), $\nu_{C=O}$ 1715 (w) and 1676 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{14}NAuO_2S$: C, 41.2; H, 3.3; N, 2.8. Found: C, 41.9; H, 3.7; N, 2.4. Mp: 226 °C with decomposition.

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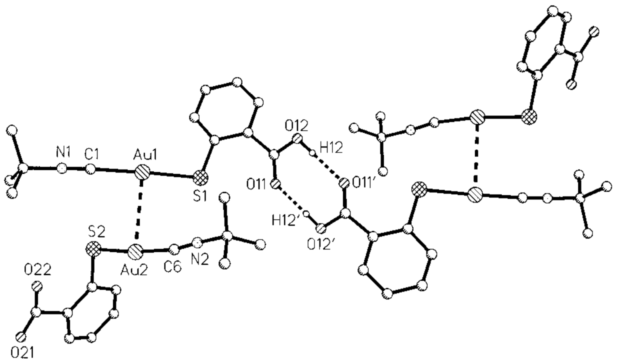

Figure 1. Tetrameric unit of **2a** aggregated via Au--Au and hydrogen bonding. Phenyl and *tert*-butyl hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1−Au2 3.157(2), Au1−C1 2.01(2), Au1−S1 2.278(5), Au2−C6 2.00(2), Au2−S2 2.274(9); C1−Au1−S1 175.5(9), C6−Au2−S2 174.5(7), S1−Au1−Au2 90.3(2), C1−Au1−Au2 87.1(8), C6−Au2−Au1 90.5(7), S2−Au2−Au1 84.1(3). Hydrogen-bonding parameters: O12-H12 0.850, H12- O11′ 1.783, O12−O11′ 2.633, O12−H12−O11′ 179.5.

of neighboring dimers are linked through bifurcated hydrogen bonding typical for carboxylic acids. These double hydrogen bridges connect crystallographically equivalent monomers related by a center of inversion coinciding with the center of the resulting eight-membered ring. Selected distances and angles are given in the caption to Figure 1. In total the lattice is composed of tetranuclear aggregates with alternating auriophilic (Au--Au) and hydrogen bonding $(O-H--O)_2$.

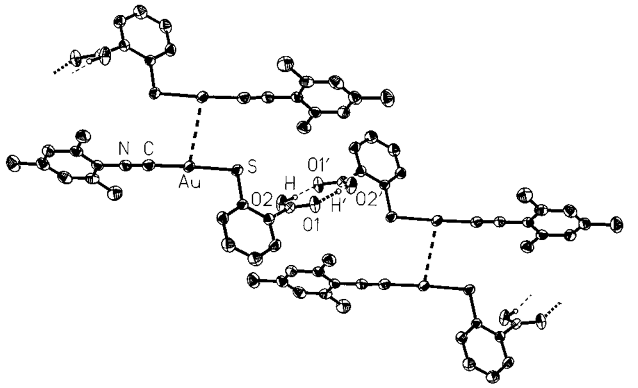

Figure 2. Four molecules of **2b** aggregated via Au--Au and hydrogen bonding as part of an extended chain. The ORTEP diagram shows 50% probability ellipsoids; phenyl and methyl hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−Au′ 3.3186(5), Au−C 1.962(4), Au−S 2.273(1); C−Au−S 175.2(1), C−Au−Au′ 99.5(1), S−Au−Au′ 83.41(3). Hydrogen-bonding parameters: O2−H 0.850, H−O1′ 1.796, O2−O1′ 2.646, O2−H−O1′ 170.8.

Compound **2b** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ formula units in the unit cell. The asymmetric unit comprises only one molecule. Two of these molecules are associated (parallel and head to tail) to form centrosymmetrical dimers through weak auriophilic bonding [Au--Au′ 3.3186(5) Å; dihedral angle S−Au−Au′−S′ 180°]. These dimers are further aggregated via bifurcated hydrogen bonding between the carboxylic acid groups to give one-dimensional polymers (Figure 2). As already pointed out for compound **2a**, the individual molecules of **2b** have a linear C−N−C−Au−S axis with normal bond distances for gold(I) isocyanide/thiolate complexes in both cases. The angles Au−S−C are also similar, with values of 105.4(1)° for **2b** and 106.4(7)°/109(1)° for **2a**.

The present results indicate that a large variety of supramolecular structures can be anticipated on the basis of combinations of hydrogen bonding with significant contributions from auriophilic interactions.

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Supporting Information Available: Tables giving the structure determination summary, atomic coordinates, isotropic and anisotropic displacement parameters, and bond distances and angles (17 pages). Ordering information is given on any current masthead page.

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(7) Crystallographic data for **2a**: $C_{12}H_{14}AuNO_2S$, fw 433.27, orthorhombic, space group *Pbca* (No. 61), $a = 11.617(2)$ Å, $b = 9.520(1)$ Å, $c = 49.548(7)$ Å, $V = 5485(1)$ Å^3, $Z = 16$, $d_{calcd} = 2.101$ g/cm^3, Enraf Nonius CAD4 diffractometer, Mo Kα radiation ($\lambda = 0.710\ 69$ Å), $T = -62$ °C, 4384 reflections measured, 4219 unique reflections of which 4206 were used. The refinement of 252 parameters converged at $wR2$ (used reflections) = 0.1936 and $R1$ [3009 observed reflections with $F_o \geq 4\sigma(F_o)$] = 0.0907. Poor crystal quality (*c*-axis!) prevented further improvements. Crystallographic data for **2b**: $C_{17}H_{16}AuNO_2S$, fw 495.33, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.575(1)$ Å, $b = 11.203(1)$ Å, $c = 12.702(2)$ Å, $\alpha = 107.03(1)$°, $\beta = 105.40(1)$°, $\gamma = 100.66(1)$°, $V = 952.43(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.727$ g/cm^3, Enraf Nonius CAD4 diffractometer, Mo Kα radiation ($\lambda = 0.710\ 69$ Å), $T = -62$ °C, 8264 reflections measured, 4096 unique reflections of which 4045 were used. The refinement of 199 parameters converged at $wR2$ (used reflections) = 0.0624 and $R1$ [3822 observed reflections with $F_o \geq 4\sigma(F_o)$] = 0.0226. The structures were solved by direct methods[8] and refined by full-matrix least-squares calculations against F^2.[9]

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